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SYNTHESIS AND EXAMINATION OF NEW CATALYTIC POLYMERS(U)  
EMORY UNIV ATLANTA GA DEPT OF CHEMISTRY F M MENGEL  
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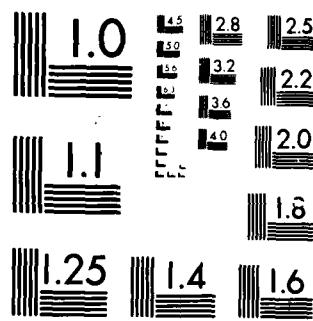
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Research supported by Grant DAAG29-82-K-0131 consisted of the following four components: (1) A new turnover catalyst capable of hydrolyzing phosphate esters under mildly basic conditions has been developed. It is currently being tested in Army laboratories. (2) A polymer-bound 4-aminopyridine has been synthesized which is capable, in the solid state, of catalyzing a variety of organic reactions. (3) A new theory for the high reactivity of		

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20. ( cont. )

intramolecular and enzymatic systems. The theory postulates that the rate of reaction between functionalities A and B is proportional to the time that A and B reside within critical distances. Attempts have been made to evaluate critical distances for organic molecules. (4) Three new multi-armed amphiphiles have been synthesized. Although these materials do not form micelles by themselves, they have the property of "seeding" micelle formation by conventional surfactants.

Dec. 1, 1985

Date

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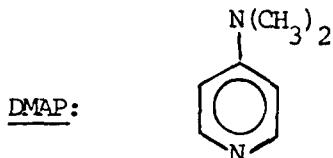
FINAL REPORT

Forward: The title of the ARO-supported project, "Synthesis and Examination of New Catalytic Polymers", describes only a small portion of the work ultimately completed and published. In addition to the polymer project, we examined new micellar turnover catalysts, sources of intramolecular and enzymatic reactivity, and new multi-armed amphiphiles. All four projects, summarized below, focus on the general problem of organic reactivity and methods of accelerating it. Since the four separate but related projects are now published (reprints are enclosed), there is no great need to reiterate many of the details. Instead, this Final Report will provide the interested reader with the major discoveries and conclusions in a concise format. Peripheral data may be secured either from the publications or by contacting the principal investigator.

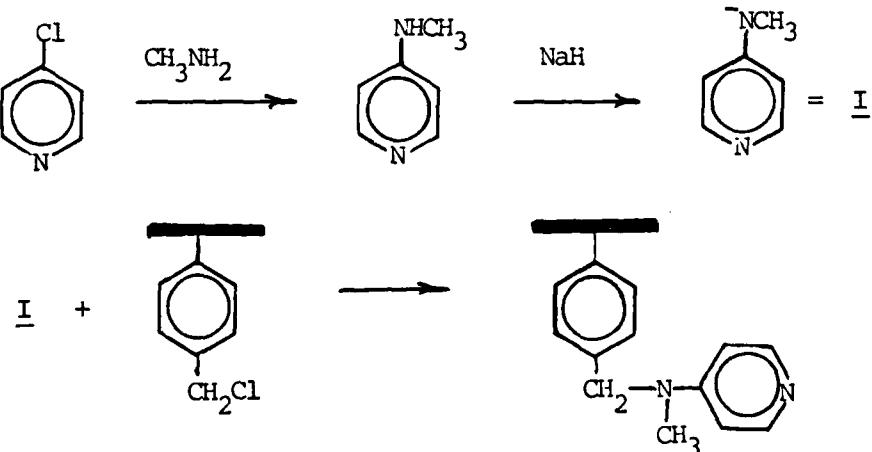
Project #1: "Synthesis and Examination of New Catalytic Polymers"

Publication: F. M. Menger and D. J. McCann, "A Polymer-Bound 4-Aminopyridine: Synthesis and Reactivity", J. Org. Chem., 1985, 50, 3928.

For over a decade 4-(dimethylamino)pyridine (DMAP) has experienced widespread use as an acylation and alkylation catalyst. DMAP is a potent nucleophile known to attack carbon, silicon, and (of particular interest for decontamination purposes) phosphorus. We have recently studied the behavior of a 4-amino pyridine grouping rendered insoluble via attachment to a polystyrene backbone.



Potential advantages of the polymer include a simple reaction workup (i.e. removal of the catalyst by filtration), recycling of "spent" (protonated) catalyst, and the development of flow systems. It is this last factor that is particularly important to Army objectives. Thus, one could visualize a shower system for army vehicles in which the waste water was pumped through filters bearing immobilized catalyst. Our synthesis of the polymer-bound catalyst is given below:



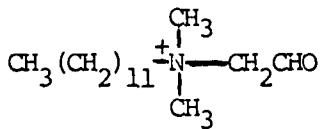
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Seven different polymer-catalyzed reactions were examined including acylations, silation, and transesterification ( see publication for details ). Each was compared with the corresponding reaction catalyzed by monomeric DMAP. It was found that monomer was somewhat more active than polymer although the differences were not huge. The polymeric catalyst might well be preferred if simple workup, catalyst recyclability, or flow systems are important considerations. Probably the most relevant contribution of this work from the standpoint of Army interests consists of a new and particularly simple synthesis of the polymer. Research groups elsewhere are examining aminopyridine catalysis in a wider variety of substrates; if this work ( partially under Army support ) proves promising, then our research will allow chemists to extend the catalytic effect to solid-state systems.

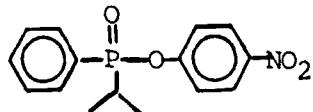
Project #2: "Development of a New Turnover Catalyst Capable of Polymerizing Carboxylic and Phosphate Esters"

Publication: F. M. Menger and L. G. Whitesell, "A Protease Mimic with Turnover Capabilities", J. Am. Chem. Soc., 1985, 107, 707.

The vast majority of organic catalysts that have been developed to cleave esters have one serious failing: the catalysts become acylated and then permanently retain the acyl group. These enzyme "models" are, therefore, stoichiometric acyl-transfer agents, not catalysts. If actual catalysis is to be achieved, acylated material must deacylate in a second and even faster step. Examples of such chemistry are rare, the most notable exception being an iodoso-containing system studied by Moss in R. A. Moss et. al., J. Am. Chem. Soc., 1983, 105, 681. We have synthesized a new catalyst, drawn below, which ( a ) forms micelles; ( b ) attacks esters in mild base where the aldehyde hydrate ionizes; ( c ) deacylates rapidly to regenerate the original aldehyde, thereby allowing



the whole process to repeat itself ( i.e. to "turnover" ). Thus, true catalysis is achieved. Samples of our catalyst have been sent to Aberdeen Proving Ground for testing by Dr. Dupont Durst, and preliminary results are now in hand. The catalyst activity was measured with a nerve agent simulant, a phosphinate ester:



In the pH range of 8-9, our catalyst splits the ester at a rate roughly an order of magnitude slower than the Moss catalyst. Thus, there is no question that we must increase the catalytic rate by a factor of 10 to rival Moss's iodosobenzene. This could conceivably be accomplished by lengthening the chain for 12 to 16. We are also currently developing "second generation" catalysts, based essentially on the chemistry of the aldehyde surfactant above, but which should have a more acidic hydroxyl. This could lower the pH at which one must operate to neutrality. It should be pointed out that although the Moss catalyst is faster than ours, we may well have the advantage in shelf-life ( iodosobenzenes are not too stable ) and in lack of toxicity.

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Project #3: "On the Source of Intramolecular and Enzymatic Reactivity"

Publication: F. M. Menger, "On the Source of Intramolecular and Enzymatic Reactivity", Accounts Chem. Res., 1985, 18, 128.

Intramolecular and enzymatic reactions often proceed  $10^8$ - $10^{10}$  times faster than intermolecular and non-enzymatic counterparts. It is extremely important for the Army—and the entire chemical and biological community for that matter—to understand the source of this amazing rate increase. Armed with such information, one can, for example, more intelligently design catalysts which rapidly decontaminate undesirable materials in the environment.

The above Accounts article addresses the question of why certain organic and biological reactions are extremely fast. It serves no purpose to reiterate the arguments in detail here—they can be found in the article. Yet it is possible to summarize here the main theme of our ideas. We postulate that: "The rate of reaction between functionalities A and B is proportional to the time that A and B reside within a critical reaction distance". In other words, reactions achieve enzyme-like rates when two reactive groups are held within certain critical distances. Attempts are made in the Accounts article to evaluate these critical distances. We estimate, for example, that holding a nucleophile within  $2.8 \text{ \AA}$  from a carbonyl group will generate an acceleration in the neighborhood of  $10^8$ . In the past, many chemists have postulated that intramolecular reactions are fast because two groups reside in "proximity" to each other. Unfortunately, the exact meaning of "proximity" was never elaborated. Our work thus represents one of the first attempts to discuss the proximity concept in a quantitative or semi-quantitative framework. Since distance is such a key parameter in solution reactivity, evaluation of the distance dependence should be major goal of physical organic chemistry in the future.

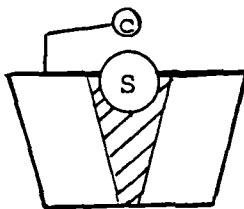
An as yet unpublished paper entitled "Nucleophilicity and Distance" will appear as part of the Symposium on Nucleophilicity organized by the ACS as part of the Chicago meeting in Sept., 1985. A preprint of this paper is available from the principal investigator on request. The manuscript discusses the following questions related to our "spatiotemporal" hypothesis:

- a. Is it reasonable to postulate a critical distance?
- b. How "critical" is the critical distance?
- c. Why is it necessary to invoke a new postulate when intramolecularity has ostensibly been already explained by entropic factors?
- d. Can the "spatiotemporal" postulate be useful in rationalizing nucleophilic behavior?
- e. What is the role of solvent in the "spatiotemporal" postulate?
- f. Is the time-distance concept not simply a "strain" theory?
- g. Is the "spatiotemporal" postulate useful in predicting chemical behavior?

It is probably easiest to envision the utility of the hypothesis by considering a specific example of relevance to the Army. The Moss iodoso catalyst, mentioned

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in the previous section, is inactive by itself. Yet in the presence of a surfactant, the catalyst is capable of rapidly destroying phosphate esters. Why is this? In terms of our postulate, the surfactant micelles serve to hold the catalyst and substrate within a critical distance. Not surprisingly, the presence of a hydrophobic tail on the catalyst and/or the substrate enhances the catalytic effect; more efficient anchoring of the reactant components within the micellar aggregate no doubt aids the rate. The question now arises: How might one improve the catalytic efficiency of micellar catalysts? No doubt the mobile nature of the micelle impacts adversely on the catalytic rates. Since a micelle is a loose and fluctuating system (with molecules entering and leaving at rapid rates and with positional changes also occurring rapidly), the time at which the two reactive components (i.e. catalyst and substrate) remain at interactive distances must be short. Thus, any further improvement in reactivity must involve a "stiffening" of the system. Ideally, the stiffened host would permanently enforce encounter distances upon the reactants. Unfortunately, since micelles are impossible to immobilize, one must search elsewhere for properly enforced residencies. One immediately thinks in this regard of a cyclodextrin; mobility within a cyclodextrin cavity is far more restrictive than in a micelle. It is this consideration which is leading us to design catalysts where a rigid cyclodextrin cavity enforces a sustained proximity upon substrate S and catalyst C:



There is, of course, a trade-off here. Sustained proximity is achieved in the cyclodextrin system by means of a more sophisticated and costly synthesis. This is an important consideration for use outside the laboratory. Furthermore, one must be certain (and this is difficult to do prior to actual experimentation) that rigid binding imparts a geometry less than the critical distance. If this is not the case, then binding could actually lead to a rate inhibition! In summary, we are waging a difficult battle: flexibility (as in a micelle) is cheap and general but deleterious to the rate; rigidity (as in a cyclodextrin) can have rate advantages but is expensive. Nature does not make things easy for us, but at least we are beginning to understand the necessary components of catalysis.

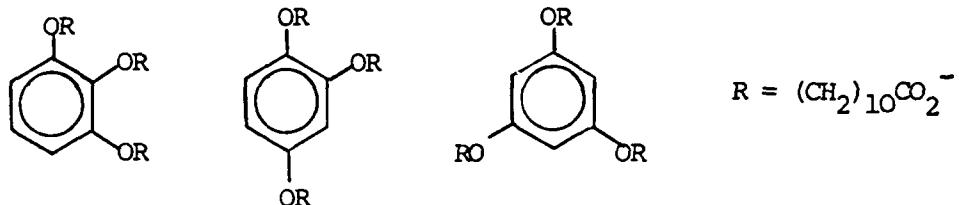
Project #4: "Synthesis and Properties of Three Triple-armed Amphiphiles"

Publication: F. M. Menger, A. J. Angel deGreiff and D. A. Jaeger, J. Chem. Soc. Chem. Commun., 1984, 543.

We are one of two research groups in the world investigating "tentacle" molecules having ion-terminated hydrocarbon chains that radiate from a central unit. Such compounds resemble "mini-micelles" in which the component surfactant chains are covalently linked. "Hexapus" was the first example of a tentacle molecule, and (more recently) we published on the "trigapus" series in a project support by ARO funding. The three compounds in the series are drawn on the next page. Classical light scattering experiments reveal the following interesting properties:

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( a ) Trigapus molecules do not form micelles; they are only weakly surface active. ( b ) When mixed at low concentrations ( 1 mM ) with conventional single-chained surfactants of opposite charge, they have a dramatic effect on both the CMC and the size of the micelles formed by the single-chained surfactant. Thus, one can readily lower the CMC of DTAB from 40 mM to 4mM! These "seeded" micelles



are, moreover, huge in size. Light scattering shows that they are at least 10 times bigger than normal. It might be possible to utilize micelle "seeding" by trigapus to lower CMC values in micelle-catalyzed systems, thereby permitting catalysis at much reduced surfactant concentrations.

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Personnel:

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